



# Investigation of Ferricinium Stability Inside the Constrained Geometry of Gold Nanotube Membranes via the Utilization of Argon Plasma



Fatih Buyukserin<sup>a,\*</sup>, Charles R. Martin<sup>b</sup>

<sup>a</sup> Department of Biomedical Engineering, TOBB University of Economics and Technology, Ankara 06560, Turkey

<sup>b</sup> Department of Chemistry and Center for Research at the Bio/Nano Interface, University of FL, Gainesville, FL 32611, USA

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## ABSTRACT

Template-synthesized gold nanotube membranes (GNMs) are versatile platforms with controllable ionic or molecular transport properties. Conductivity and transport across these membranes can be tuned by applying electronic or chemical modification strategies. In a previous study, we have reported the modulation of cationic transport through GNMs by chemisorbing a ferrocene (Fc)-linked alkyl thiol to gold surface films, as well as to the nanotube walls. The modulation was achieved by controlling the oxidation state of Fc, but it degraded with time as  $Fc^+$  is not stable in aqueous medium, and the extent of modulation varied with nanotube diameter. Herein, we present the dependence of  $Fc^+$  decay on the nanotube diameter of GNMs. For this purpose, it was necessary to remove the Fc-thiol monolayers from gold surface films and leave the Fc-thiol groups lining the nanotube walls intact. This was achieved by applying a mild argon plasma treatment to both faces of a Fc-thiol-modified GNM sample. Our results suggest that for all cases, the  $Fc^+$  decay obeys first order decay kinetics and as the nanotube diameter increases, the  $Fc^+$  decay becomes faster and it resembles a flat surface-like decay pattern. We suspect that the hydrophobic character of the Fc-thiol within the constrained nanotube environment and differing counterion tendencies toward this milieu play roles in this observation.

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## 1. Introduction

We have been investigating a general method for preparing nanomaterials called template synthesis [1–3] that involves the deposition of a desired material within the pores of a nanoporous membrane or other solid. Using this method, a new class of synthetic membranes, namely gold nanotube membranes (GNMs), was developed. This material contains monodisperse gold nanotubes with controllable diameters that can be as small as 1 nm [4]. The gold nanotubes span the complete thickness of the membrane and can be modified to tune the molecular or ionic transport across them [5–10]. Gold nanotubes with conical shapes, which are heavily used for biosensing applications, can also be produced by starting with the appropriate polymeric template [11]. We have been using these GNMs to investigate how pore size, charge and chemistry affect conductivity and transport selectivity in such membranes [5–10]. Of particular relevance to the work reported here, ion and chemical transport selectivity can be successfully

introduced and modulated by chemisorbing thiols to the gold nanotube walls [5,7,9].

In a related previous study, we have reported an alternative method for electromodulating ion transport in GNMs [12]. This method involves the modification of gold nanotubes with an alkyl thiol that contains a redox-active ferrocene (Fc) substituent. With this membrane system, the charge density on the nanotube walls can be electromodulated Faradaically by using the potential applied to the GNM to control the position of equilibrium for the following redox reaction [13–16]:



We have found that when the nanotube-bound Fc is oxidized, the flux of a cationic permeate species through the membrane is suppressed compared to the flux where the Fc is reduced. However, the flux difference between these states is lost with membrane use because when the Fc is present in the  $Fc^+$  state, it is susceptible to nucleophilic attack and decomposition [17]. The extent of  $Fc^+$  decomposition is directly related to the strength of the nucleophile [18] and it is a first order decay in aqueous solutions [19].

In this paper, we further explore this decay and illustrate the effect of nanotube size on  $Fc^+$  decomposition. For this purpose, it was necessary to remove the Fc-thiol on gold surface films and

\* Corresponding author.

E-mail address: [fbuyukserin@etu.edu.tr](mailto:fbuyukserin@etu.edu.tr) (F. Buyukserin).

leave the Fc-thiol monolayers lining the gold nanotube walls. This was accomplished by briefly (30 s) exposing both faces of the membrane to a mild argon plasma treatment, which was shown to be effective for removing surface coatings in similar membrane systems [20]. Following the plasma application, the decay of  $\text{Fc}^+$  was investigated in membranes of different nanotube diameters and it was compared to the decay in a commercial gold button electrode. The results suggest that the decay rate increases with increasing nanotube diameter and in all cases it is found to obey first order decay kinetics. Furthermore, the decay pattern resembles a surface-like decay as the nanotube diameter of the membrane increases.

## 2. Experimental methods

### 2.1. Materials

Polycarbonate membranes (with 30, 50, 200 and 600 nm diameter pores) were obtained from Osmonics Inc.  $\text{SnCl}_2$  was used as received from Aldrich, as ethanol (absolute) from Aaper, 11-ferrocenyl-1-undecanethiol from Dojindo Chemicals,  $\text{KClO}_4$ ,  $\text{AgNO}_3$  and trifluoroacetic acid from Acros Organics. A commercial gold-plating solution (Oromerse SO Part B, involves  $\sim 0.3$  M aqueous  $\text{Na}_3\text{Au}(\text{SO}_3)_2$ ) was obtained from Technic Inc., RI, USA.  $\text{Na}_2\text{SO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{OH}$ ,  $\text{HNO}_3$ , methanol and formaldehyde were obtained from Fisher and used as received. Purified water was attained through a Millipore, Milli-Q system.

### 2.2. Electroless Gold Deposition

Polycarbonate template membranes with the above-mentioned initial pore diameters were subjected to electroless deposition to obtain GNMs [21]. Here, the template polycarbonate filter membrane was first immersed into methanol (5 min) and then into a solution that was 0.025 M in  $\text{SnCl}_2$  and 0.07 M in trifluoroacetic acid (45 min), which results in the Sn-sensitized form of the membrane [22]. The membrane was then immersed into a 0.029 M aqueous ammoniacal  $\text{AgNO}_3$  solution (7.5 min) and then rinsed with methanol (5 min). After these steps, the membrane was

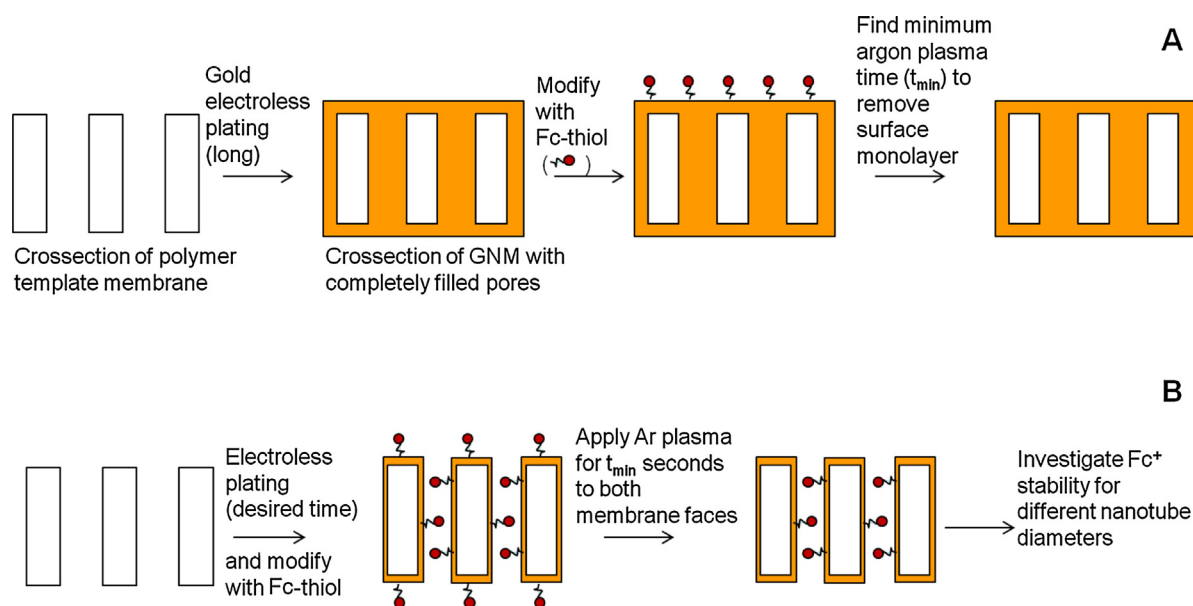
treated with a gold-plating bath, which was prepared by mixing 0.5 mL of the commercial gold-plating solution with 20 mL of an aqueous solution that was 0.127 M in  $\text{Na}_2\text{SO}_3$ , 0.625 M in formaldehyde, and 0.025 M in  $\text{NaHCO}_3$ . Here, the pH of the gold-plating bath was adjusted to 10 by 1 M  $\text{H}_2\text{SO}_4$  and its temperature was kept constant at 4 °C during the electroless deposition. Membranes of different nanotube diameters were prepared by varying the deposition time within the gold plating bath [5,23].

The diameters of the gold nanotubes in GNMs were determined using the gas-flux measurement described previously [5] for diameters  $< 50$  nm. Regarding nanotubes with larger diameters, electron micrographs of the membranes obtained via Hitachi S4000 FE-SEM were used to calculate the average nanotube diameter. GNMs with nanotube diameters  $10 \pm 2.0$ ,  $28 \pm 2.6$ ,  $65 \pm 7.5$ , and  $284 \pm 20$  nm were used in this work.

### 2.3. Sample Preparation and Thiol Modification

When a porous polymeric template membrane is subjected to electroless metal deposition, two different gold surfaces form: (i) the gold layer on the inside walls of the nanotubes, and (ii) the gold surface films on both faces of the membrane [22]. The gold surfaces were used to make electrical contact by applying copper tape with a conductive adhesive (3 M, #1181) to the outer edge of one gold surface film [22]. Because the membrane sample is the working electrode in electrochemical experiments, the end of the copper tape protruding from the membrane was used as the electrode lead. To prepare the GNM sample, it was sandwiched between two pieces of an insulating plastic tape (3 M, Scotch brand no. 375) that also covered the conductive tape used to make the electrical contact to the sample. Each piece of the insulating tape had a  $0.2 \text{ cm}^2$ -area hole punched through it, and the holes were aligned on either side of the membrane.

The thiol used for the membrane modification was 11-ferrocenyl-1-undecanethiol (Fc-thiol). Here, gold nanotube walls and gold surface films were subjected to chemisorption by mounting the assembled membrane sample between the two halves of a U-tube setup [5,8], where both half-cells were filled



**Fig. 1.** The rationale behind the use of argon plasma. GNMs with filled pores were modified with Fc-thiol and investigated by CV and XPS to find the minimum argon etching time to remove Fc-thiol from gold surface film (A). The same etching conditions were then applied to GNMs with desired nanotube diameters to explore  $\text{Fc}^+$  stability (B).

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